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(54) Title: CABLE-SHEATHING COMPOSITION			
(57) Abstract			
<p>A cable-sheathing composition and its use as outer sheath for a power cable or a communication cable are disclosed. The cable-sheathing composition is a multimodal, preferably bimodal, mixture of olefin polymers, preferably ethylene plastics, having a density of about 0.915-0.955 g/cm<sup>3</sup> and a melt flow rate of about 0.1-0.3 g/10 min, said olefin polymer mixture comprising at least a first and a second olefin polymer, of which the first has a density and a melt flow rate selected from (a) about 0.930-0.975 g/cm<sup>3</sup> and about 50-2000 g/10 min and (b) about 0.88-0.93 g/cm<sup>3</sup> and about 0.1-0.8 g/10 min. Preferably, the olefin polymer mixture has been obtained by coordination-catalysed polymerisation of at least one <math>\alpha</math>-olefin in several stages, preferably two stages consisting of a loop reactor/a gas-phase reactor or a gas-phase reactor/a gas-phase reactor, through polymerisation or copolymerisation of ethylene in the first stage and copolymerisation of ethylene with butene, 4-methyl-1-pentene, 1-hexene or 1-octene in the second stage.</p>			

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CABLE-SHEATHING COMPOSITION

The present invention relates to a cable-sheathing composition, as well as the use thereof as outer sheathing for a power cable or a communication cable.

Cables, by which is meant power cables for high voltage, medium voltage or low voltage, and communication cables, such as optical cables, coaxial cables and pair cables, generally comprise a core surrounded by a sheath consisting of one or more layers. The outermost layer is referred to as outer sheath or sheathing layer and is nowadays made of polymer material, preferably ethylene plastic. The highly diverse fields of application for various sorts of cables, such as telecommunication cables, including conventional copper cables and fibre-optical cables, as well as power cables, entail that the sheathing material has to meet a number of property requirements which in some respects are contradictory. Thus, important properties of cable-sheathing materials are good processability, i.e. it should be easy to process the material within a broad temperature range, low shrinkage, high mechanical strength, high surface finish as well as high environmental stress cracking resistance (ESCR). Since it has hitherto been difficult or even impossible to meet all these property requirements, prior-art sheathing materials have been the result of compromise, such that that good properties in one respect have been obtained at the cost of poorer properties in some other respect.

Thus, it would be highly advantageous if this compromise as regards the properties of cable-sheathing materials could be reduced or even eliminated. In particular, it would be advantageous if one were able to improve the ESCR of the material and reduce the shrinkage at a given processability.

The present invention achieves this goal by a cable-sheathing composition which, instead of the unimodal polyethylene plastic used in conventional cable-sheathing compositions, consists of a multimodal olefin polymer mixture having certain given values of density and melt flow rate, both as regards the polymer mixture and as regards the polymers forming part thereof.

The present invention thus provides a cable-sheathing composition, which is characterised in that it consists of a multimodal olefin polymer mixture having a density of about 0.915-0.955 g/cm<sup>3</sup> and a melt flow rate of about 0.1-0.3 g/10 min, said olefin polymer mixture comprising at least a first and a second olefin polymer, of which the first has a density and a melt flow rate selected from (a) about 0.930-0.975 g/cm<sup>3</sup> and about 50-2000 g/10 min and (b) about 0.88-0.93 g/cm<sup>3</sup> and about 0.1-0.8 g/10 min.

The invention further concerns the use of this cable-sheathing composition as outer sheath for a power cable or a communication cable.

Further distinctive features and advantages of the invention will appear from the following description and the appended claims.

However, before the invention is described in more detail, a few key expressions will be defined.

By the "modality" of a polymer is meant the structure of the molecular-weight distribution of the polymer, i.e. the appearance of the curve indicating the number of molecules as a function of the molecular weight. If the curve exhibits one maximum, the polymer is referred to as "unimodal", whereas if the curve exhibits a very broad maximum or two or more maxima and the polymer consists of two or more fractions, the polymer is referred to as "bimodal", "multimodal" etc. In the following, all polymers whose molecular-weight-distribution curve is very broad or has more than one maximum are jointly referred to as "multimodal".

The "melt flow rate" (MFR) of a polymer is determined in accordance with ISO 1133, condition 4, and is equivalent to the term "melt index" previously used. The melt flow rate, which is indicated in g/10 min, is an indication of the flowability, and hence the processability, of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer.

By the term "environmental stress cracking resistance" (ESCR) is meant the resistance of the polymer to crack formation under the action of mechanical stress and a reagent in the form of a surfactant. The ESCR is determined in accordance with ASTM D 1693 A, the reagent employed being Igepal CO-630.

By the term "ethylene plastic" is meant a plastic based on polyethylene or on copolymers of ethylene, the ethylene monomer making up most of the mass.

As indicated in the foregoing, the cable-sheathing composition according to the invention is distinguished by the fact that it consists of a multimodal olefin polymer mixture of specified density and melt flow rate.

It is previously known to produce multimodal, in particular bimodal, olefin polymers, preferably multimodal ethylene plastics, in two or more reactors connected in series. As instances of this prior art, mention may be made of EP 040 992, EP 041 796, EP 022 376 and WO 92/12182, which are hereby incorporated by way of reference as regards the production of multimodal polymers. According to these references, each and every one of the polymerisation stages can be carried out in liquid phase, slurry or gas phase.

According to the present invention, the main polymerisation stages are preferably carried out as a combination of slurry polymerisation/gas-phase polymerisation or gas-phase polymerisation/gas-phase polymerisation. The slurry polymerisation is preferably performed in a so-called loop reactor. The use of slurry polymerisation in a stirred-tank reactor is not preferred in the present

invention, since such a method is not sufficiently flexible for the production of the inventive composition and involves solubility problems. In order to produce the inventive composition of improved properties, a flexible method is required. For this reason, it is preferred that the composition is produced in two main polymerisation stages in a combination of loop reactor/gas-phase reactor or gas-phase reactor/gas-phase reactor. It is especially preferred that the composition is produced in two main polymerisation stages, in which case the first stage is performed as slurry polymerisation in a loop reactor and the second stage is performed as gas-phase polymerisation in a gas-phase reactor. Optionally, the main polymerisation stages may be preceded by a prepolymerisation, in which case up to 20% by weight, preferably 1-10% by weight, of the total amount of polymers is produced. Generally, this technique results in a multimodal polymer mixture through polymerisation with the aid of a chromium, metallocene or Ziegler-Natta catalyst in several successive polymerisation reactors. In the production of, say, a bimodal ethylene plastic, which according to the invention is the preferred polymer, a first ethylene polymer is produced in a first reactor under certain conditions with respect to monomer composition, hydrogen-gas pressure, temperature, pressure, and so forth. After the polymerisation in the first reactor, the reaction mixture including the polymer produced is fed to a second reactor, where further polymerisation takes place under other conditions. Usually, a first polymer of high melt flow rate (low molecular weight) and with a moderate or small addition of comonomer, or no such addition at all, is produced in the first reactor, whereas a second polymer of low melt flow rate (high molecular weight) and with a greater addition of comonomer is produced in the second reactor. As comonomer, use is commonly made of other olefins having up to 12 carbon atoms, such as  $\alpha$ -olefins having 3-12 carbon atoms, e.g. propene, butene, 4-methyl-

1-pentene, hexene, octene, decene, etc., in the copolymerisation of ethylene. The resulting end product consists of an intimate mixture of the polymers from the two reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or two maxima, i.e. the end product is a bimodal polymer mixture. Since multimodal, and especially bimodal, polymers, preferably ethylene polymers, and the production thereof belong to the prior art, no detailed description is called for here, but reference is had to the above specifications.

It should here be pointed out that, in the production of two or more polymer components in a corresponding number of reactors connected in series, it is only in the case of the component produced in the first reactor stage and in the case of the end product that the melt flow rate, the density and the other properties can be measured directly on the material removed. The corresponding properties of the polymer components produced in reactor stages following the first stage can only be indirectly determined on the basis of the corresponding values of the materials introduced into and discharged from the respective reactor stages.

Even though multimodal polymers and their production are known per se, it is not, however, previously known to use such multimodal polymer mixtures in cable-sheathing compositions. Above all, it is not previously known to use in this context multimodal polymer mixtures having the specific values of density and melt flow rate as are required in the present invention.

As hinted at above, it is preferred that the multimodal olefin polymer mixture in the cable-sheathing composition according to the invention is a bimodal polymer mixture. It is also preferred that this bimodal polymer mixture has been produced by polymerisation as above under different polymerisation conditions in two or more

polymerisation reactors connected in series. Owing to the flexibility with respect to reaction conditions thus obtained, it is most preferred that the polymerisation is carried out in a loop reactor/a gas-phase reactor, a gas-phase reactor/a gas-phase reactor or a loop reactor/a loop reactor as the polymerisation of one, two or more olefin monomers, the different polymerisation stages having varying comonomer contents. Preferably, the polymerisation conditions in the preferred two-stage method are so chosen that a comparatively low-molecular polymer having a moderate, low or, which is preferred, no content of comonomer is produced in one stage, preferably the first stage, owing to a high content of chain-transfer agent (hydrogen gas), whereas a high-molecular polymer having a higher content of comonomer is produced in another stage, preferably the second stage. The order of these stages may, however, be reversed.

Preferably, the multimodal olefin polymer mixture in accordance with the invention is a mixture of propylene plastics or, which is most preferred, ethylene plastics. The comonomer or comonomers in the present invention are chosen from the group consisting of  $\alpha$ -olefins having up to 12 carbon atoms, which in the case of ethylene plastic means that the comonomer or comonomers are chosen from  $\alpha$ -olefins having 3-12 carbon atoms. Especially preferred comonomers are butene, 4-methyl-1-pentene, 1-hexene and 1-octene.

In view of the above, a preferred ethylene-plastic mixture according to the invention consists of a low-molecular ethylene homopolymer mixed with a high-molecular copolymer of ethylene and butene, 4-methyl-1-pentene, 1-hexene or 1-octene.

The properties of the individual polymers in the olefin polymer mixture according to the invention should be so chosen that the final olefin polymer mixture has a density of about 0.915-0.955 g/cm<sup>3</sup>, preferably about 0.920-0.950 g/cm<sup>3</sup>, and a melt flow rate of about



0.1-3.0 g/10 min, preferably about 0.2-2.0 g/10 min. According to the invention, this is preferably achieved by the olefin polymer mixture comprising a first olefin polymer having a density of about 0.930-0.975 g/cm<sup>3</sup>,  
5 preferably about 0.955-0.975 g/cm<sup>3</sup>, and a melt flow rate of about 50-2000 g/10 min, preferably about 100-1000 g/10 min, and most preferred about 200-600 g/10 min, and at least a second olefin polymer having such a density and such a melt flow rate that the olefin polymer mixture  
10 obtains the density and the melt flow rate indicated above.

If the multimodal olefin polymer mixture is bimodal, i.e. is a mixture of two olefin polymers (a first olefin polymer and a second olefin polymer), the first olefin  
15 polymer being produced in the first reactor and having the density and the melt flow rate indicated above, the density and the melt flow rate of the second olefin polymer, which is produced in the second reactor stage, may, as indicated in the foregoing, be indirectly determined  
20 on the basis of the values of the materials supplied to and discharged from the second reactor stage.

In the event that the olefin polymer mixture and the first olefin polymer have the above values of density and melt flow rate, a calculation indicates that the second  
25 olefin polymer produced in the second stage should have a density in the order of about 0.88-0.93 g/cm<sup>3</sup>, preferably 0.91-0.93 g/cm<sup>3</sup>, and a melt flow rate in the order of about 0.01-0.8 g/10 min, preferably about 0.05-0.3 g/10 min.

30 As indicated in the foregoing, the order of the stages may be reversed, which would mean that, if the final olefin polymer mixture has a density of about 0.915-0.955 g/cm<sup>3</sup>, preferably about 0.920-0.950 g/cm<sup>3</sup>, and a melt flow rate of about 0.1-3.0 g/10 min, preferably  
35 ably about 0.2-2.0 g/10 min, and the first olefin polymer produced in the first stage has a density of about 0.88-0.93 g/cm<sup>3</sup>, preferably about 0.91-0.93 g/cm<sup>3</sup>, and

a melt flow rate of 0.01-0.8 g/10 min, preferably about 0.05-0.3 g/10 min, then the second olefin polymer produced in the second stage of a two-stage method should, according to calculations as above, have a density in the order of about 0.93-0.975 g/cm<sup>3</sup>, preferably about 0.955-0.975 g/cm<sup>3</sup>, and a melt flow rate of 50-2000 g/10 min, preferably about 100-1000 g/10 min, and most preferred about 200-600 g/10 min. This order of the stages in the production of the olefin polymer mixture according to the invention is, however, less preferred.

In order to optimise the properties of the cable-sheathing composition according to the invention, the individual polymers in the olefin polymer mixture should be present in such a weight ratio that the aimed-at properties contributed by the individual polymers are also achieved in the final olefin polymer mixture. As a result, the individual polymers should not be present in such small amounts, such as about 10% by weight or below, that they do not affect the properties of the olefin polymer mixture. To be more specific, it is preferred that the amount of olefin polymer having a high melt flow rate (low-molecular weight) makes up at least 25% by weight but no more than 75% by weight of the total polymer, preferably 35-55% by weight of the total polymer, thereby to optimise the properties of the end product.

The inventive, multimodal olefin polymer mixture described above can be produced in other ways than by polymerisation in two or more polymerisation reactors connected in series, even though this is especially preferred in accordance with the invention. In one alternative aspect of the invention, the multimodal olefin polymer mixture is produced by blending in a melted state of the individual polymers to form part of the olefin polymer mixture. Such melt blending is preferably brought about by coextrusion of the individual polymers, thereby resulting in a mechanical mixture. Since it is difficult, in such melt blending, to achieve satisfactory homogeneity

ty with the final olefin polymer mixture, this way of producing the multimodal olefin polymer mixture is less preferred than the above, preferred method involving polymerisation in polymerisation reactors connected in series.

The use of multimodal olefin polymer mixtures of the type described above results in inventive cable-sheathing compositions having much better properties than conventional cable-sheathing compositions, especially as regards shrinkage, ESCR and processability. In particular the reduced shrinkage of the inventive cable-sheathing composition is a great advantage.

As indicated in the foregoing, the cable-sheathing composition according to the invention can be used for producing outer sheaths for cables, including power cables as well as communication cables. Amongst power cables, whose outer sheaths may advantageously be produced from the cable-sheathing composition according to the invention, mention may be made of high-voltage cables, medium-voltage cables and low-voltage cables. Amongst communication cables, whose outer sheaths may advantageously be made from the cable-sheathing composition according to the invention, mention may be made of pair cables, coaxial cables and optical cables.

Here follows a few non-restricting Examples intended to further elucidate the invention and its advantages.

#### Example 1

In a polymerisation plant consisting of a loop reactor connected in series to a gas-phase reactor and involving the utilisation of a Ziegler-Natta catalyst, a bimodal ethylene plastic was polymerised under the following conditions.

#### The First Reactor (Loop Reactor)

In this reactor, a first polymer (Polymer 1) was produced by the polymerisation of ethylene in the presence of hydrogen (molar ratio of hydrogen to ethylene

= 0.38:1). The resulting ethylene homopolymer had an MFR value of 492 g/10 min and a density of 0.975 g/cm<sup>3</sup>.

The Second Reactor (Gas-Phase Reactor)

In this reactor, a second polymer (Polymer 2) was produced by the polymerisation of ethylene and butene (molar ratio in the gas phase of butene to ethylene = 0.22:1, of hydrogen to ethylene = 0.03:1). The resulting copolymer of ethylene and butene was present in the form of an intimate mixture with the ethylene homopolymer from the first reactor, the weight ratio of Polymer 1 to Polymer 2 being 45:55.

The bimodal mixture of Polymer 1 and Polymer 2 had a density of 0.941 g/cm<sup>3</sup> and an MFR value of 0.4 g/10 min. After compounding with carbon black, one obtained an end product containing 2.5% by weight thereof, resulting in a final density of 0.951 g/cm<sup>3</sup>. This end product will in the following be referred to as Bimodal Ethylene Plastic 1.

Bimodal Ethylene Plastic 1 was used as cable-sheathing composition, and the properties of this composition were determined and compared with those of a conventional cable-sheathing composition of unimodal ethylene plastic (Reference 1). Reference 1 had a density of 0.941 g/cm<sup>3</sup> (after compounding to a carbon-black content of 2.5% by weight and a density of 0.951 g/cm<sup>3</sup>) and an MFR value of 0.24 g/10 min.

In this Example, as well as the following Examples, the shrinkage of the composition produced was determined in accordance with a method (in the following referred to as UNI-5079) which had been developed in order to evaluate the shrinkage tendency of sheathing materials. The shrinkage is determined in the following manner.

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Cable samples for the evaluation are extruded as follows.

Conductor:	3.0 mm solid, Al conductor
Wall thickness:	1.0 mm
5 Temperature, die:	+210°C or +180°C
Distance between die and water bath:	35 cm
Temperature, water bath:	+23°C
Line velocity:	75 m/min
10 Die type:	Semi-tube
Nipple:	3.65 mm
Die:	5.9 mm
Screw design:	Elise
Breaking plate	

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The shrinkage in per cent is measured after 24 h in a room with constant temperature (+23°C) as well as after 24 h at a temperature of +100°C.

20 Cable samples measuring approximately 40 cm are measured. Conveniently, the cable sample is so marked that measurement after the conditionings can be carried out at the same point on the cable sample.

25 Should the sample be found to shrink during measurement, marks of about 40 cm first have to be made. Then, the length is cut and remeasured. Double samples are taken of each cable that is to be analysed. The samples are placed in the room with constant temperature for 24 h, whereupon they are measured, and the shrinkage value in per cent is calculated.

30 All the samples are then placed on a talcum bed at +100°C for 24 h. The samples are then measured, and the total shrinkage value in per cent is calculated on the basis of the initial length.

35 The measurement results are indicated in Table 1 below.

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Table 1

Material properties		Bimodal 1	Reference 1
5	Tensile break strength (MPa) <sup>1</sup>	34	38
	Elongation at break(%) <sup>1</sup>	800	900
	ESCR <sup>2</sup>	0/2000 h	F20/550 h
	Shrinkage (%) at		
10	23°C/24 h <sup>3</sup>	0.0	0.7
	23°C/24 h <sup>4</sup>	0.0	0.7
	Shrinkage (%) at		
	100°C/24 h <sup>3</sup>	1.0	2.0
	100°C/24 h <sup>4</sup>	0.9	2.3
15	<u>Surface finish</u> <sup>5</sup>		
	After extrusion at		
	180°C at		
	15 m/min	0-1	0
20	35 m/min	0-1	0
	75 m/min	0	0
	140 m/min	0	1
	After extrusion at		
	210°C at		
25	15 m/min	-	0
	35 m/min	0-1	0
	75 m/min	0-1	0
	140 m/min	0	0-1
30	1: Determined in accordance with ISO 527-2 1993/5A on cable samples.		
	2: Determined in accordance with ASTM D 1693/A, 10% Igepal. The results are indicated as the percentage of cracked sample rods at a given time. F20 means		
35	that 20% of the sample rods were cracked after the time indicated.		
	3: Determined in accordance with UNI-5079 after extrusion at 180°C.		

4: Determined in accordance with UNI-5079 after extrusion at 210°C.

5: Classification: 0 = excellent to 4 = very uneven.

It is evident from the values indicated in Table 1 that the inventive sheathing material exhibits improved properties as regards shrinkage, especially at room temperature, and environmental stress cracking resistance (ESCR). The tensile-strength properties of the sheathing material according to the invention are on a level with those of Reference 1. Also the processability, which can be deduced from the MFR value, of the sheathing material according to the invention is as good as that of Reference 1. It should be emphasised that, whereas the sheathing material of Reference 1 has good processing properties obtained at the cost of poor shrinkage properties, especially at room temperature, the sheathing material according to the invention has good processing properties as well as good (low) shrinkage properties. This is a considerable advantage, which is enhanced by the improved ESCR properties of the sheathing material according to the invention.

#### Example 2

In the polymerisation plant of Example 1, a bimodal ethylene plastic was produced under the following conditions.

#### The First Reactor (Loop Reactor)

In this reactor, a first polymer (Polymer 1) was produced by the polymerisation of ethylene in the presence of hydrogen (molar ratio of hydrogen to ethylene = 0.38:1). The resulting ethylene homopolymer had an MFR value of 444 g/10 min and a density of 0.975 g/cm<sup>3</sup>.

#### The Second Reactor (Gas-Phase Reactor)

In this reactor, a second polymer (Polymer 2) was produced by the polymerisation of ethylene and butene (molar ratio of butene to ethylene = 0.23:1; molar ratio of hydrogen to ethylene = 0.09:1). The resulting copolymer of ethylene and butene was present in the form of an

intimate mixture with the ethylene homopolymer from the first reactor, the weight ratio of Polymer 1 to Polymer 2 being 40:60.

5 The bimodal mixture of Polymer 1 and Polymer 2, which constituted the end product, had a density of 0.941 g/cm<sup>3</sup> (after an addition of 2.5% by weight of carbon black, 0.951 g/cm<sup>3</sup>) and an MFR value of 1.4 g/10 min. In the following, this end product will be referred to as Bimodal Ethylene Plastic 2.

10 In similar fashion, yet another bimodal ethylene plastic was produced (in the following referred to as Bimodal Ethylene Plastic 3), the molar ratio of hydrogen to ethylene in the first reactor being 0.39:1, and the resulting ethylene homopolymer (Polymer 1) in the first  
15 reactor having an MFR value of 468 g/10 min and a density of 0.962 g/cm<sup>3</sup>. In the second reactor, a copolymer of ethylene and butene (Polymer 2) was produced, the molar ratio of butene to ethylene being 0.24:1, and the molar ratio of hydrogen to ethylene being 0.07:1. The weight  
20 ratio of Polymer 1 to Polymer 2 was 45:55. The end product (Bimodal Ethylene Plastic 4) had a density of 0.941 g/cm<sup>3</sup> (after compounding with 2.5% by weight of carbon black, 0.951 g/cm<sup>3</sup>) and an MFR value of 1.3 g/10 min.

25 Bimodal Ethylene Plastic 2 and Bimodal Ethylene Plastic 3 were used as cable-sheathing compositions, and the properties of these compositions were determined and compared with those of a prior-art sheathing composition (Reference 2). Reference 2 was a special composition  
30 intended for use in cases where particularly low shrinkage is required, such as fibre-optical applications, and this composition consisted of a melt blend of a polyethylene fraction having a density of 0.960 g/cm<sup>3</sup> and an MFR value of 3.0 g/10 min, and another polyethylene frac-  
35 tion having a density of 0.920 g/cm<sup>3</sup> and an MFR value of 1.0 g/10 min. This resulted in an end product having a density of 0.943 g/cm<sup>3</sup> (after an addition of 2.5% by



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weight of carbon black, 0.953 g/cm<sup>3</sup>) and an MFR value of 1.7 g/10 min.

The results of the measurements of the properties of the three cable-sheathing compositions are indicated in Table 2 below.

Material properties	<u>Table 2</u>		
	Bimodal ethylene plastic	Reference 2	
	2	3	
Tensile break strength (MPa) <sup>1</sup>	32	30	32
Elongation at break (%) <sup>1</sup>	900	890	1150
ESCR <sup>2</sup>	0/2000 h	0/2000 h	F20/190 h
Shrinkage (%) at 23°C/24 h <sup>4</sup>	0.0	0.0	0.1
Shrinkage (%) at 100°C/24 h <sup>4</sup>	0.8	1.0	0.8
<u>Surface finish</u> <sup>5</sup>			
After extrusion at 210°C at			
15 m/min	2	2	3
35 m/min	1-2	1	4
75 m/min	0-1	0	4
140 m/min	0-1	0	4

1: Determined in accordance with ISO 527-2 1993/5A.

2: Determined in accordance with ASTM D 1693/A, 10%

Igepal. The results are indicated as the percentage of cracked sample rods at a given time. F20 means that 20% of the sample rods were cracked after the given time.

4: Determined in accordance with UNI-5079 after extrusion at 210°C.

5: Classification: 0 = excellent to 4 = very uneven.

As is evident from Table 2, the prior-art special sheathing material (Reference 2) has good shrinkage properties at room temperature. However, the shrinkage properties of Reference 2 have been achieved at the cost of poor processing properties, as appears from, inter alia, the poor values of surface finish. Generally, the sheathing material of Reference 2 can only be processed within a narrow "process window", i.e. within narrow ranges as regards the processing parameters. In contrast to Reference 2, the sheathing materials according to the invention (Bimodal Ethylene Plastic 2 and 3) exhibit as good shrinkage properties as Reference 2 while presenting better processing properties (broader process window) involving a better surface finish of the cable sheath. Furthermore, the sheathing materials according to the invention exhibit much better environmental stress cracking resistance (ESCR) and also present good tensile break strength.

#### Example 3

In the polymerisation plant used in Examples 1 and 2, a bimodal polyethylene plastic (Ethylene Plastic 4) was produced under the following conditions.

#### The First Reactor (Loop Reactor)

In this reactor, a first polymer (Polymer 1) was produced by the polymerisation of ethylene in the presence of 1-butene and hydrogen gas (molar ratio 1-butene:hydrogen gas:ethylene = 1.74:0.22:1). Polymer 1 had an MFR value of 310 g/10 min and a density of 0.939 g/cm<sup>3</sup>.

#### The Second Reactor (Gas-Phase Reactor)

The polymer from the loop reactor was transferred to the gas-phase reactor, where further polymerisation of ethylene with 1-butene in the presence of hydrogen gas was carried out (molar ratio 1-butene:hydrogen gas:ethylene = 0.80:0.02:1), resulting in a new polymer component (Polymer 2). The weight ratio of Polymer 1 to Polymer 2 was 42:58. The MFR value of the re-

sulting end product was 0.3 g/10 min, and the density was 0.922 g/cm<sup>3</sup>.

Excellent mechanical properties, good ESCR as well as good shrinkage properties were achieved also in this case, where both polymer components contain 1-butene as comonomer, as is evident from Table 3 below.

Table 3

Material properties	Ethylene plastic 4
10 Tensile break strength	25,9 MPa
Elongation at break	905%
ESCR	0/2000 h
Shrinkage % 23°C/24 h	0%
100°C/24 h	0%

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Example 4

A bimodal ethylene plastic (Ethylene Plastic 5) was produced by extrusion in a laboratory extruder of the type Buss-Kokneter of a dry-mixed granulate consisting of 47 parts by weight of an HD polyethylene having a density of 0.968 g/cm<sup>3</sup> and an MFR value of 500 g/10 min, as well as 53 parts by weight of an LLDPE having a density of 0.925 g/cm<sup>3</sup> and an MFR value of 0.10 g/10 min. In addition, 2000 ppm of Irganox B 225FF was added as stabiliser. The temperature of the screw was 80°C and that of the cylinder was 140°C. The resulting mixture had a density of 0.949 g/cm<sup>3</sup> and an MFR value of 0.9 g/10 min. Otherwise, the material (no admixture of carbon black) exhibited the following qualities:

Table 4

<u>Material properties</u>		<u>Ethylene plastic 5</u>
	Tensile break strength	36.3 MPa
5	Elongation at break	883%
	ESCR	0/2000 h
	Shrinkage % 23°C/24 h	0%
	100°C/24 h	1.0%
10	<u>Surface finish</u>	
	After extrusion at	
	210°C at	
	15 m/min	2
	35 m/min	0-1
15	75 m/min	0
	140 m/min	0

This extruded mixture (Ethylene Plastic 5) thus presented values of mechanical properties, shrinkage, ESCR and surface finish which are comparable to those of bimodal materials produced in reactors connected in series.

## CLAIMS

1. A cable-sheathing composition, c h a r a c -  
5 t e r i s e d in that it consists of a multimodal olefin  
polymer mixture having a density of about 0.915-0.955 g/  
cm<sup>3</sup> and a melt flow rate of about 0.1-0.3 g/10 min,  
said olefin polymer mixture comprising at least a first  
and a second olefin polymer, of which the first has a  
10 density and a melt flow rate selected from (a) about  
0.930-0.975 g/cm<sup>3</sup> and about 50-2000 g/10 min and (b)  
about 0.88-0.93 g/cm<sup>3</sup> and about 0.1-0.8 g/10 min.
2. A cable-sheathing composition as claimed in claim  
1, c h a r a c t e r i s e d in that the first olefin  
15 polymer has a density of about 0.930-0.975 g/cm<sup>3</sup> and a  
melt flow rate of about 50-2000 g/10 min.
3. A cable-sheathing composition as claimed in claim  
1 or 2, c h a r a c t e r i s e d in that the olefin  
polymer mixture has a density of about 0.920-0.950 g/cm<sup>3</sup>  
20 and a melt flow rate of about 0.2-2.0 g/10 min, and  
that the first olefin polymer has a density of about  
0.955-0.975 g/cm<sup>3</sup> and a melt flow rate of about  
100-1000 g/10 min.
4. A cable-sheathing composition as claimed in any  
25 one of claims 1-3, c h a r a c t e r i s e d in that the  
olefin polymer mixture is a mixture of ethylene plastics.
5. A cable-sheathing composition as claimed in any  
one of claims 1-4, c h a r a c t e r i s e d in that it  
has been obtained by polymerisation of at least one  
30  $\alpha$ -olefin in more than one stage.
6. A cable-sheathing composition as claimed in claim  
5, c h a r a c t e r i s e d in that it has been obtained  
by coordination-catalysed polymerisation in at least two  
stages of ethylene and, in at least one stage, an  $\alpha$ -ole-  
35 fin comonomer having 3-12 carbon atoms.
7. A cable-sheathing composition as claimed in claim  
6, c h a r a c t e r i s e d in that the polymerisation

stages have been carried out as slurry polymerisation, gas-phase polymerisation or a combination thereof.

8. A cable-sheathing composition as claimed in claim 7, characterised in that the slurry polymerisation has been carried out in a loop reactor.

9. A cable-sheathing composition as claimed in claim 8, characterised in that the polymerisation has been carried out in a loop-reactor/gas-phase-reactor process in at least one loop reactor followed by at least one gas-phase reactor.

10. A cable-sheathing composition as claimed in any one of claims 1-4, characterised in that it has been obtained by melt blending of different ethylene plastics.

11. A cable-sheathing composition as claimed in any one of the preceding claims, characterised in that it is a bimodal mixture of ethylene plastics.

12. A cable-sheathing composition as claimed in claim 11, characterised in that the first ethylene plastic makes up 25-75% by weight of the total amount of polymers in the composition.

13. The use of the cable-sheathing composition as claimed in any one of the preceding claims as outer sheath for a power cable.

14. The use of the cable-sheathing composition as claimed in any one of claims 1-12 as outer sheath for a communication cable.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 96/00900

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 23/04, C08F 10/00, H01B 3/30

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08L, C08F, H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4547551 A (FAY W. BAILEY ET AL), 15 October 1985 (15.10.85), table 1, abstract --	1-4, 10-14
A	WO 9510548 A1 (FINA RESEARCH S.A.), 20 April 1995 (20.04.95), page 3, paragraph 3, table 1 --	1-9, 11-14
A	EP 0533160 A1 (PHILLIPS PETROLEUM COMPANY), 24 March 1993 (24.03.93), page 8, abstract --	1-4, 10-14
A	WO 9212182 A1 (NESTE OY), 23 July 1992 (23.07.92), page 1, line 8 - line 29, examples 1, 4, 5 and 6, page 10 --	1-9, 11-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

\* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

14 October 1996

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 96/00900

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0318841 A2 (QUANTUM CHEMICAL CORPORATION), 7 June 1989 (07.06.89), page 2 - page 3, table 1  --	1-4, 10-14
A	EP 0237294 A2 (NIPPON OIL CO. LTD.), 16 Sept 1987 (16.09.87), page 2, line 3 - line 56, table 1  -- -----	1-9, 11-14



## INTERNATIONAL SEARCH REPORT

Information on patent family members

01/10/96

International application No.

PCT/SE 96/00900

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4547551	15/10/85	CA-A- 1216392 EP-A,B- 0100843 SE-T3- 0100843 JP-B- 4029695 JP-A- 59047242 US-A- 4461873	06/01/87 22/02/84  19/05/92 16/03/84 24/07/84
WO-A1- 9510548	20/04/95	BE-A- 1005271 GB-A,B- 2273894 JP-T- 8504883	15/06/93 06/07/94 28/05/96
EP-A1- 0533160	24/03/93	JP-A- 5194796 US-A- 5380803	03/08/93 10/01/95
WO-A1- 9212182	23/07/92	AT-T- 130316 DE-D,T- 69114696 EP-A,B- 0517868 SE-T3- 0517868 ES-T- 2079844 JP-T- 5504786 NO-B- 179286 US-A- 5326835	15/12/95 11/04/96 16/12/92  16/01/96 22/07/93 03/06/96 05/07/94
EP-A2- 0318841	07/06/89	CA-A- 1301391 JP-A- 1213346 US-A- 4840996	19/05/92 28/08/89 20/06/89
EP-A2- 0237294	16/09/87	DE-A- 3774905 JP-B- 7025829 JP-A- 62207307 US-A- 5013802	16/01/92 22/03/95 11/09/87 07/05/91